Thermoelectric Power of the Iodine Complexes of Aromatic Diamines and Thiazines

Mizuka SANO*, Koichi OHNO**, and Hideo AKAMATU***

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

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The thermoelectric power of *N*,*N'*-diphenyl-*p*-phenylenediamine$\cdot I_2$, *N*,*N'*-di-*β*-naphthyl-*p*-phenylenediamine$\cdot I_{3.5}$, phenothiazine$\cdot I_3$, and *N*-methylphenothiazine$\cdot I_3$ was measured in the temperature range from −35 to 140°C. The observed power for each complex was explained by means of the mechanism of mixed conduction of electrons with holes, and the ratio of electron-conduction to hole-conduction was estimated as a function of temperature. In the iodine complexes of the substituted *p*-phenylenediamines the conductivity due to electrons is found to be larger than that due to holes, while in phenothiazine$\cdot I_3$ holes contribute more to the conductivity. In *N*-methylphenothiazine$\cdot I_3$, the hole-conduction is predominant in the higher temperature region and the electron-conduction in the lower temperature region.

Solid electron-donor-acceptor complexes, particularly those involving appreciable contribution from the dative structures, exhibit interesting electric and magnetic properties. *N*,*N'*-diphenyl-*p*-phenylenediamine (DPPD),[1,2] *N*,*N'*-di-*β*-naphthyl-*p*-phenylenediamine (DNPD),[1] phenothiazine (PT),[3], and *N*-methylphenothiazine (MPT)[3] have been reported to form stable iodine complexes. The crystal structure analysis of the iodine complex of DPPD has shown that the iodine atoms are stacked in columns perpendicular to the *ac* plane, and the donor molecules are arranged in layers 3.77 Å apart.[4] The iodine columns are coordinated to NH groups of the donor. The infrared spectrum of phenothiazine-iodine complex has been reported to be identical with that of semiquinoid phenazathionium bromide, indicating that the ground state of the solid complex is dative.[3]

The magnetic properties of these iodine complexes have been reported.[1] They are either diamagnetic or weakly paramagnetic at room temperature. After corrections are made for the diamagnetic contribution and for the paramagnetic one due to paramagnetic impurities, the intrinsic paramagnetic susceptibility is found to decrease slightly with the decrease in temperature. The exchange coupling constant *J* between ionradicals in a solid has values of 0.05 eV for DPPD$\cdot I_2$, 0.08 for DNPD$\cdot I_{3,5}$, 0.04 for MPT$\cdot I_3$, and over 0.1 for PT$\cdot I_3$.

These complexes show high electrical conductivity but neither photoconductivity nor Hall voltage, so that only the measurement of thermoelectric power seems to be a reliable means of determining the type of conduction. In this paper we present the results on the thermoelectric power measurement of the complexes and an estimation of the ratio of electron-conduction to hole-conduction in the solid.

Experimental

DPPD$\cdot I_2$, dark green crystals with metallic lustre were obtained by mixing benzene solutions of the diamine and iodine in the stoichiometric ratio. (Found: C, 42.86; H, 3.40; N, 5.70%. Calcd for $C_{18}H_{16}N_2I_2$: C, 42.05; H, 3.14; N, 5.45%).

DNPD$\cdot I_{3.5}$, dark brownish black crystalline powder precipitated on addition of a benzene solution of iodine to a benzene solution of the diamine (Found: C, 38.97; H, 2.17; N, 3.46%. Calcd for $C_{26}H_{20}N_2I_{3,5}$: C, 38.81; H, 2.51; N, 3.48%).

PT$\cdot I_3$ was prepared by mixing benzene solutions of the components in the stoichiometric ratio.[3] MPT$\cdot I_3$ was prepared from an ether solution.

A sample powder was sandwiched in a Teflon holder between small disks of platinum supported by two copper cylinders. Each platinum disk was insulated electrically from the copper cylinder with a piece of Teflon sheet. The powder was pressed under the pressure of 100 kg/cm^2 with an aid of a lever. Thickness of the sample was adjusted to 0.2—0.5 cm. The junctions of copper-constantan thermocouples were soldered to the platinum disks.

Cylindrical electric heaters attached to the upper and lower portions of the copper cylinders were controlled to provide temperature gradient in a sample. For measurements below room temperature the copper cylinders were cooled with dry ice cubes. By this arrangement the temperature dependence of thermoelectric power could be measured in the range from −35 to 140°C. Reference junctions connected to the thermocouples were insulated electrically from one another and placed in an ice-water bath maintained at 0°C.

The thermo-electromotive force (emf) of a sample observed through the copper leads of the thermocouples and that of each thermocouple were measured potentiometrically by use of suitable switching systems. The thermoelectric power *Q* is calculated by the relation.

$$Q = \Delta V/\Delta T, \qquad (1)$$

where ΔV represents the thermo-emf generated in the sample-platinum-copper circuit by the temperature difference ΔT between the sample-platinum junctions. The average temperature of the junctions is taken to be the temperature of sample.

The electrical conductivity of the same sample specimen packed in the Teflon holder was measured by the *DC* method as a function of temperature. The temperature of the specimen was controlled with the aid of a third electric heater in conjunction with a dry ice cooling bath.

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* Present address: Department of Materials Science, The University of Electro-Communications, Chofu, Tokyo.

** Present address: The Institute for Solid State Physics, The University of Tokyo, Azabu, Tokyo.

*** Present address: Institute of Materials Science and Engineering, Yokohama National University, Minato-ku, Yokohama.

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Results

All the complexes showed high absorption coefficients in the visible and near-infrared spectral regions. The absorption peaks, though broad and poorly defined, were found around 2.2, 1.7, and 1.1 μ for PT·I_3, MPT·I_3, and DPPD·I_2, respectively. The peaks in the near-infrared region are characteristic of solid ionradical salts with strong exchange coupling between ionradical components.[5]

The complexes gave rise to thermo-emf in the order of 10^{-3} V between the platinum electrodes for a temperature difference of about 10°. The absolute thermoelectric power of the complexes was obtained by correcting for the value for copper.[6] The power of each complex was found to be constant at a fixed sample temperature, being independent of the amount of provided temperature gradient around 10° and of the thickness of the sample. Good reproducibility of power was obtained by the rise and fall of temperature within the temperature range. The iodine complex of 4,4′-bis(dimethylamino)-diphenylamine (DADA), however, showed no reproducible power when it was heated up to 40°C.

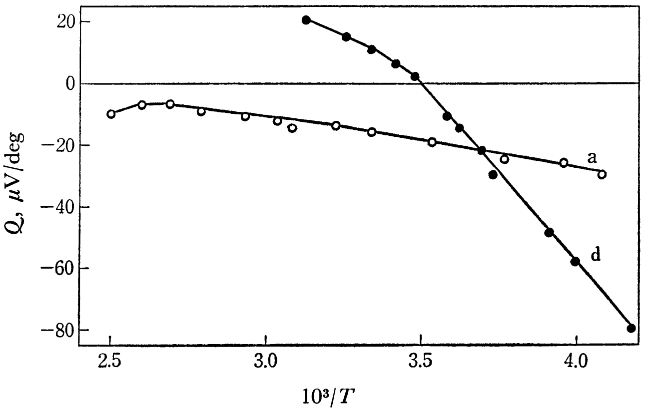

Fig. 1. Thermoelectric powers for (a) DPPD·I_2 and (d) MPT·I_3.

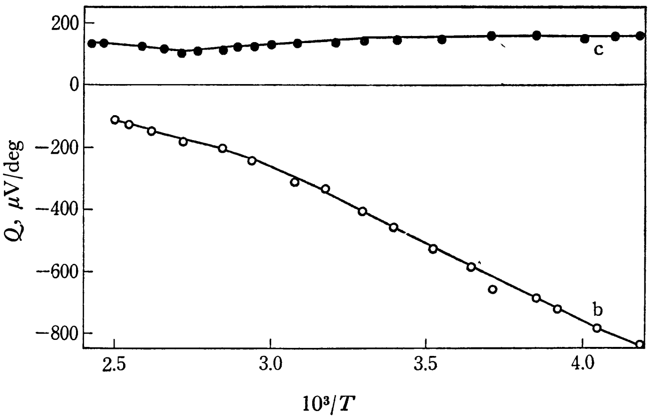

Fig. 2. Thermoelectric powers for (b) DNPD·$I_{3.5}$ and (c) PT·I_3.

Values for the power at 15°C are summarized in Table 1. The sign of power refers to the sign of developed emf at the cold junction. The power for DPPD·I_2, DNPD·$I_{3.5}$, and MPT·I_3 was found to decrease with falling temperature, while that for PT·I_3 changed little with temperature change. The temperature dependence of power is shown in Figs. 1 and 2.

The logarithm of conductivity σ was found to be proportional to the reciprocal of temperature $1/T$ in the entire temperature region, and the activation energy for conduction E_a could be calculated by the formula

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right). \tag{2}$$

The activation energy and specific resistivity ρ at 15°C are summarized in Table 1.

TABLE 1. THERMOELECTRIC POWER AND SPECIFIC RESISTIVITIES AT 15°C, AND ACTIVATION ENERGIES FOR CONDUCTION

	Q (μV/deg)	ρ (Ω·cm)	E_a (eV)
DPPD·I_2	−20	3.5×10	0.095
DNPD·$I_{3.5}$	−540	5×10^4	0.37
DADA·I	−860	1.3×10^5	—
PT·I_3	+150	1.7×10	0.164
MPT·I_3	+3	2.3×10^2	0.14

Discussion

Johnson and Lark-Horovitz derived the following formula (Eq. (24) in Ref. 7) as a general expression for thermoelectric power of a band-model semiconductor.[7]

$$Q = -\frac{k}{e(n_1c+n_2)}\left[A(n_1c-n_2) - n_1c\ln\left\{\frac{n_1h^3}{2(2\pi m_1kT)^{3/2}}\right\} + n_2\ln\left\{\frac{n_2h^3}{2(2\pi m_2kT)^{3/2}}\right\}\right], \tag{3}$$

where n_1 and n_2 are the densities and m_1 and m_2 the effective masses of conduction electron and hole, respectively. c denotes the mobility ratio μ_1/μ_2, and A the scattering parameter. The parameter comes from the energy of transferring average carrier, and varies somewhat with the scattering process. Scattering theory predicts this quantity varies from 2 for neutral scattering centers to 4 for ionic centers.[8]

In the case where only one type of carrier is present, the expression for the power is obtained from Eq. (3) by dropping the terms pertaining to another type of carrier. Thus we get for electrons

$$Q = -\frac{k}{e}\left[A - \ln\left\{\frac{n_1h^3}{2(2\pi m_1kT)^{3/2}}\right\}\right]. \tag{4}$$

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Within the limitation of the Boltzmann distribution, the carrier density n_1 can be related to the Fermi level ζ by the equation

$$n_1 = \frac{2(2\pi m_1 kT)^{3/2}}{h^3}\exp\left(-\frac{\varepsilon_1{}^0-\zeta}{kT}\right), \tag{5}$$

where $\varepsilon_1{}^0$ is the energy at the bottom of the conduction band. Substituting Eq. (5) into Eq. (4), we obtain

$$Q = -\frac{k}{e}\left[\frac{\varepsilon_1{}^0-\zeta}{kT}+A\right]. \tag{6}$$

The expression for the power only by holes is given by

$$Q = +\frac{k}{e}\left[\frac{\zeta-\varepsilon_2{}^0}{kT}+A\right], \tag{7}$$

where $\varepsilon_2{}^0$ is the energy at the top of the valence band.

Substitution of both densities of electron and hole into Eq. (3) gives the following expression for mixed conduction of electrons with holes.

$$Q = -\frac{k}{e}\left[\frac{(x-1)}{(x+1)}\left(\frac{E_g}{2kT}+A\right)+\frac{(\varepsilon_1{}^0-\zeta)-(\zeta-\varepsilon_2{}^0)}{2kT}\right], \tag{8}$$

where x denotes the conductivity ratio $n_1\mu_1/n_2\mu_2$, and E_g the forbidden band width.

Explanation of the experimentally obtained curve of the power for each complex was undertaken by means of the formula for the carriers of only one type, on the assumption that the energy difference between the Fermi level and the conduction band $\varepsilon_1{}^0-\zeta$ or the valence band $\zeta-\varepsilon_2{}^0$ is equal to the observed activation energy of conduction E_a. Only the formula including the value of A with negative sign is found to represent the observed power. Theory does not allow a negative A value, so that this type of conduction is ruled out.

In a triethylammonium(TCNQ)$_2$ single crystal the sign of the majority of carriers has been reported to be negative along the c-crystal axis and positive along the a-axis.[9] The result suggests a mixed contribution from both types of carriers to the conductivity in ionradical crystals.

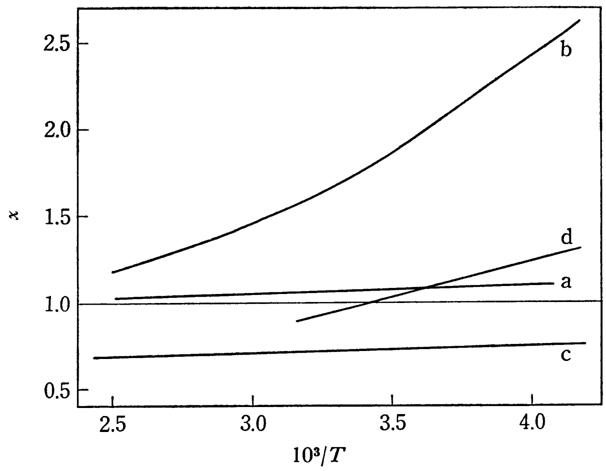

Fig. 3. Conductivity ratios for (a) DPPD·I$_2$, (b) DNPD·I$_{3.5}$, (c) PT·I$_3$, and (d) MPT·I$_3$.

Comparing the expression for mixed conduction Eq. (8) with the experimentally obtained curve on the assumption that for an ionradical solid the value of A equals 4, as found for ionic scattering centers in ionic crystals, and that the last term in Eq. (8) is negligibly small compared with the first one, one can estimate the conductivity ratio x, and thus determine the type of conduction. In this analysis twice the value for E_a is used for E_g. The conductivity ratio thus obtained is shown in Fig. 3 as a function of temperature. If the electron density n_1 is taken to be equal to the hole density n_2, the value for x corresponds to the mobility ratio μ_1/μ_2. This condition, however, does not seem to hold in the entire range of temperature.

The x values for DPPD·I$_2$ and DNPD·I$_{3.5}$ are greater than unity, indicating that the conductivity due to electrons is larger than that due to holes. The x-value smaller than unity for PT·I$_3$ indicates that holes contribute more to the conductivity in the complex. In MPT·I$_3$, on the other hand, the hole-conduction is predominant in the higher temperature region and the electron-conduction in the lower temperature region. The change of x-value with temperature seems to arise mainly from the different dependence of electron and hole mobilities on temperature.

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